Dielectric Relaxation in Ferroelectrics

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By

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Abstract

The frequency and temperature dependences of the complex dielectric constants, the Cole-Cole plots and the dielectric loss tangents of extended order-disorder type ferroelectrics are calculated with the aid of a new dispersion formula. The different types of the real dielectric constant versus temperature such as $NaNO_2$, Ca_2Sr $(C_2H_5CO_2)_6$ and KD_2PO_4 are elucidated by the monodispersive formula with a parameter c which gives a measure for deviation from the Debye type. The results agree with experiments, and the comparisons between the formula and other formulas are made also.

I. Introduction

In recent years there has been an increasing interest in the dynamical aspects of the critical phenomena. In this paper, we have studied the frequency and temperature dependences of the complex dielectric constant of extended order-disorder type ferroelectrics. The complex dielectric constants $\varepsilon=\varepsilon'-i\varepsilon''$ are classified into three types by empirically: (A) the real part of the constant ε' has a dip near the Curie temperature T_c and ε' $(T_c)\simeq 0$ such as the case of $NaNO_2$[1,2]; (B) the ε' has a dip near T_c and $\varepsilon'(T_c)>0$ such as the case of $Ca_2Sr(C_2H_5CO_2)_6$[3]; (C) the ε' has a peak near T_c such as the case of KD_2PO_4.[4,5] In 1947, Mason[6] investigated the dielectric relaxation phenomena in Rochelle salt with the aid of Eyring's[7] theory of absolute reaction rates who have obtained the complex dielectric constant as

$$\varepsilon(\omega)-\varepsilon_\infty=\frac{\varepsilon_0-\varepsilon_\infty}{1+i\omega\tau}, \tag{1}$$

where

$$\varepsilon_0-\varepsilon_\infty=\frac{C}{|T-T_C|}, \tag{2}$$

$$\tau\propto(\varepsilon_0-\varepsilon_\infty)\exp(\Delta U/kT), \tag{3}$$

here ω is the angular frequency, τ is the relaxation time, C is the Curie constant, ΔU is the potential barrier between two stable orientations of the dipole, and ε_∞ and ε_0 are the dielectric constants in high and low frequency limits, respectively. Usually, the value of C in the ferroelectric phase is the one half of the paraelectric phase's value. This Debye

type dispersion formula holds good for the type (A). The Mason theory has only one relaxation time, then the theory is called a monodispersive theory, the Cole-Cole polt of which is the Debye circle.

Hill and Ichiki have measured the complex dielectric constant of KD_2PO_4[4,5] and TGS[5,8] and interpreted their results assuming a Gaussian distribution of relaxation times. Their complex dielectric constant takes the form

$$\varepsilon(\omega)-\varepsilon_\infty=\int_0^\infty \frac{y(\tau)}{1+i\omega\tau}\,d\tau\,, \tag{4}$$

where the distribution function $y(\tau)$ takes a Gaussian type such as

$$y(\tau)=A\ \exp\ \{-(\tau/\tau_0)^2\};\ (A:\ \text{a constant})\,, \tag{5}$$

with

$$\tau_0=1/\alpha(T-T_C)\,, \tag{6}$$

where α is the proportionality constant which is determined empirically. If we put $\omega=0$ with $A=2\alpha C/\sqrt{\pi}$ in (4), then we have the Curie-Weiss law (2). The real part of this complex dielectric constant has a peak at the Curie temperature which consist with the type (C). They have interpreted that the distribution of the relaxation times would arise from a distribution of clusters of different sizes where dipoles tend to have a particular orientation. Although this explanation of polydispersion is very interesting, we can not understand why the theory can not account for the type (A) or (B) and recent experiments[9,10] show that the results of TGS can be well explained by a monodispersive theory rather than the polydispersive theory.

The first attempt to deal with the three types in a unified manner has been made by Matsubara and Yoshimitsu,[11,12] their phenomenological theory gives a Cole-Cole[13] type:

$$\varepsilon(\omega)-\varepsilon_\infty=\frac{\varepsilon_0-\varepsilon_\infty}{1+(i\omega\tau)^{\beta_{MY}}}\ ;\quad (0<\beta_{MY}\leq 1)\,, \tag{7}$$

where β_{MY} is the polydispersive parameter. The case $\beta_{MY}=1$ reduces to the Mason theory, the case $0<\beta_{MY}\leq 1/2$ is similar to the type (C) and the case $1/2<\beta_{MY}<1$ corresponds to the type (B). The incline angle θ of the Cole-Cole plot circle is expressed as

$$\theta=\frac{\pi}{2}(1-\beta_{MY})\,, \tag{8}$$

which can be determined by experiment.

Nakamura et al.[14] have pointed out that the Cole-Cole plot curves of Hill and Ichiki's data are not circular arcs but lemniscates. Ishibashi, Sawada and Takagi[15] found that the data are well explained by the Davidson-Cole[16] dispersion formula

$$\varepsilon(\omega)-\varepsilon_\infty=\frac{\varepsilon_0-\varepsilon_\infty}{(1+i\omega\tau)^\nu}\ ;\ (0<\nu\leq 1)\,, \tag{9}$$

which gives a lemniscate-like Cole-Cole plot. This dispersion formula has been derived from

the response function of $e^{-t/\tau}t^{\nu-1}$ by them.[15] Ishibashi and Takagi[17] have criticized Hill and Ichiki's assumption of Gaussian distribution of relaxation times according to the investigation of the relation between the distribution and the dispersion formula (9).

Another empricial formula has been given by Nakamura and Ishida[18] who have pointed out that the observed complex dielectric constants can not be represented by (7) and they have showed that the observed values conform to the empirical formula such as

$$\varepsilon(\omega)-\varepsilon_\infty = \frac{\varepsilon_0-\varepsilon_\infty}{1+i^{\beta_{\mathrm{NI}}}\omega\tau}\ ;\ (0<\beta_{\mathrm{NI}}\leq 1)\,. \tag{10}$$

Very recently Gesi[19] has indicated that this dispersion formula can be obtained by replacing τ in (1) by a complex one $\tau^*=\tau\exp(i\phi)$ with the phase factor $\phi=\pi/2(1-\beta_{\mathrm{NI}})$.

One of the authors† has proposed the dispersion formula of the form

$$\varepsilon(\omega) = \frac{\varepsilon_0}{1+i\omega(\tau-i\gamma')}\,, \tag{11}$$

where γ' is assumed as

$$\gamma' = \gamma_0'/|T-T_C|\,. \tag{12}$$

Here γ_0' is the positive parameter and for simplicity the high frequency limit dielectric constant ε_∞ has been neglected. We can classify the three types (A), (B) and (C) by the theory with the parameter γ_0'.

An interpolation dispersion formula for order-disorder [type (A)], extended order-disorder [types (B) and (C)] and displacive ferroelectrics has been proposed heuristically by one of the authors.[20] This formula takes the form:

$$\varepsilon(\omega)-\varepsilon_0 = \frac{\varepsilon_0-\varepsilon_\infty}{2}\Bigg[\left\{\frac{1+i\omega_{\mathrm{p1}}\tau_{\mathrm{p1}}}{1+i(\omega+\omega_{\mathrm{p1}})\tau_{\mathrm{p1}}}+\frac{1-i\omega_{\mathrm{p1}}\tau_{\mathrm{p1}}}{1+i(\omega-\omega_{\mathrm{p1}})\tau_{\mathrm{p1}}}\right\}$$
$$+d\frac{\omega}{|\omega|}\left\{\frac{1+i\omega_{\mathrm{p2}}\tau_{\mathrm{p2}}}{1+i(\omega+\omega_{\mathrm{p2}})\tau_{\mathrm{p2}}}-\frac{1-i\omega_{\mathrm{p2}}\tau_{\mathrm{p2}}}{1+i(\omega-\omega_{\mathrm{p2}})\tau_{\mathrm{p2}}}\right\}\Bigg], \tag{13}$$

where τ_{p1} and τ_{p2} are the relaxation time, ω_{p1} and ω_{p2} are the imaginary part of the reciprocal complex relaxation time (for the extended order-disorder type) or the frequency (for the displacive type), and d is the parameter which measures the deviation from the displacive type. This formula (13) contains various cases as follows:

[I] $\omega_{p1}=0$ and $\omega_{p2}=0$, or $\omega_{p1}=0$ and d=0; order-disorder type. This case reduces to the Debye type or Mason's dispersion formula (1).

[II] d=1, $\tau_{p1}=\tau_{p2}$ and $\omega_{p1}=\omega_{p2}$; extended order-disorder type.

When $\omega\geq 0$ the dispersion formula (13) reduces to:

$$\varepsilon(\omega)-\varepsilon_\infty = \frac{(\varepsilon_0-\varepsilon_\infty)(1+i\omega_{\mathrm{p}}\tau_{\mathrm{p}})}{1+i(\omega+\omega_{\mathrm{p}})\tau_{\mathrm{p}}} \tag{14}$$

† M. Inoue: Annual Meeting of the Physical Society of Japan, April, 1972.

[III] d=0; displacive or resonance type.

This case reduces to the resonance type dispersion formula.[21]

The dispersion formula (10) and (11) satisfy the Kramers -Krönig relation but they contradict with a symmerty relation of $\varepsilon^*(\omega)=\varepsilon(-\omega)$. On the other hand, the dispersion formula (13) satisfies both the relations. In section II we study in detail the frequency and temperature dependences of the complex dielectric constants, the Cole-Cole plots and dielectric loss tangents for the case [II]. Section III is devoted to discussions and some remarks.

II. Frequency and Temperature Dependences of the Complex Dielectric Constant

Some essential aspects of critical phenomena are characterized by the critical indexes and considerable studies of the indexes has been made in magnetic systems. However, studies of the indexes for ferroelectrics are still at a rather rudimentary stage compared to that of magnetics. One of the reasons is that the Curie-Weiss law can be applied to the region of near the ferroelectric transition point, namely in ferroelectrics the width of the critical region is very narrow.

In our case the quantities ε_0, τ_p and ω_p usually behave anomalously near the Curie temperature T_c, then we introduce the critical indexes γ, Δ and Δ' such that

$$(\varepsilon_0-\varepsilon_\infty)\simeq CT_c^{-1}|(T-T_c)/T_c|^{-\gamma} \quad ; \gamma>0\,, \tag{15}$$

$$\tau_p\simeq\tau_{p0}|(T-T_c)/T_c|^{-\Delta} \quad ; \Delta>0\,, \tag{16}$$

$$\omega_p\simeq\omega_{p0}|(T-T_c)/T_c|^{\Delta'} \quad ; \Delta'>0\,, \tag{17}$$

where τ_{p0} and ω_{p0} are some constants which usually proportional to C and C^{-1}, respectively.

In this section, we confine ourselves to the case [II], namely extended order-disorder type, and $\omega\geq 0$, therefore the general dispersion formula (13) reduces to (14). According to the experiments[1-5], we can safely assume that the critical index of the denominator is equal to that of the numerator in both the real and imaginary parts of the right hand side of the formula (14), therefore, we obtain

$$\gamma=\Delta=\Delta'\,. \tag{18}$$

In this case, we can classify the three types by a parameter c such that

$$c=0 \quad ; \text{type } (A)\,, \tag{19}$$

$$0<c<1 \quad ; \text{type } (B)\,, \tag{20}$$

$$c\geq 1 \quad ; \text{type } (C)\,, \tag{21}$$

where the parameter c is defined by

$$c\equiv\omega_p\tau_p\,. \tag{22}$$

The real dielectric constant and the imaginary dielectric constant of (14) versus temperature at several values of c with fixed $\omega\tau_{p0}$ are shown in Fig. 1 and 2, respectively. Figure 1 shows that the real dielectric constant sensitively depends on the value of c and

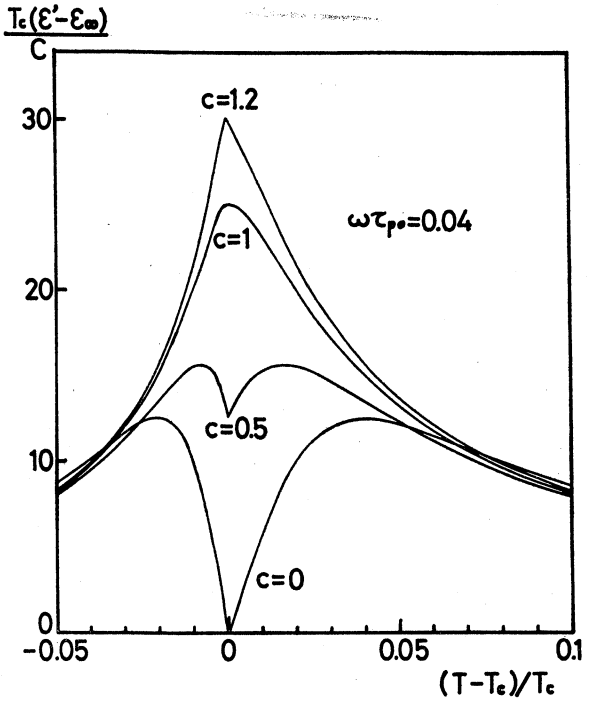

Fig. 1. The real dielectric constant versus temperature at several values of c.

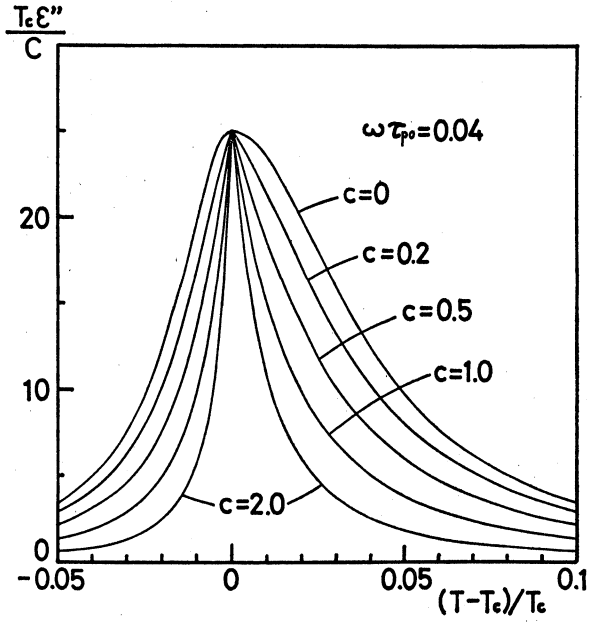

Fig. 2. The imaginary dielectric constant versus temperature at several values of c.

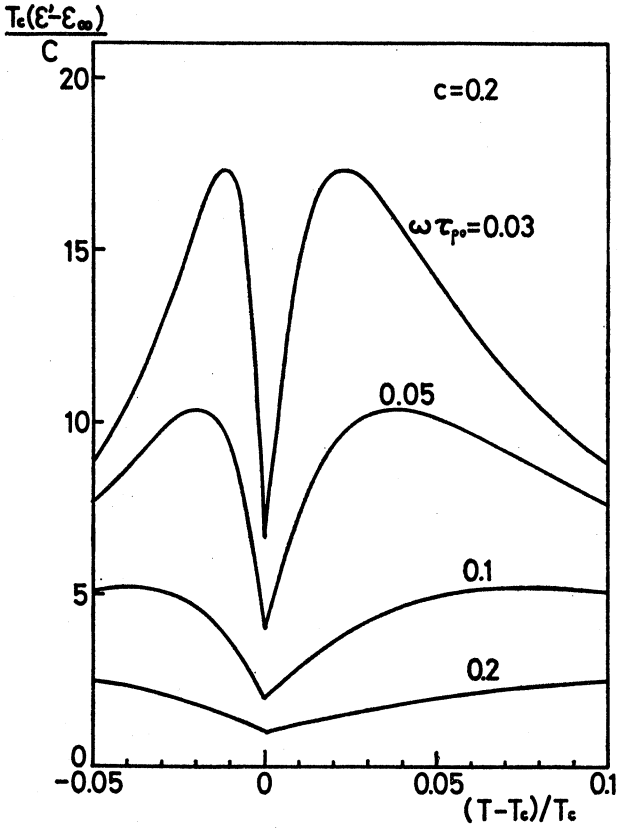

Fig. 3. The real dielectric constant versus temperature at several values of $\omega\tau_{p0}$.

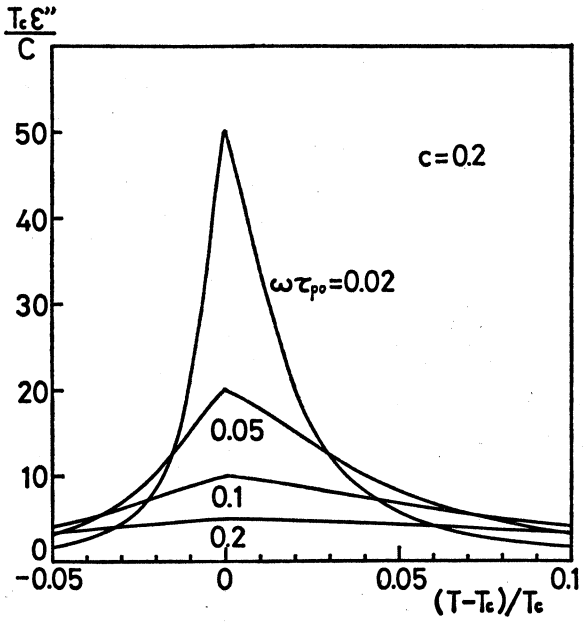

Fig. 4. The imaginary dielectric constant versus temperature at several values of $\omega\tau_{p0}$.

the different types (A), (B) and (C) can be described by the formula (14). On the contrary, the imaginary dielectric constant slightly depends on c as in Fig. 2. Similarly, the temperature dependence of the real and imaginary parts of the dielectric constant for different frequencies with c fixed are shown in Fig. 3 and 4, respectively. The maximum value of $T_c\,(\varepsilon'-\varepsilon_\infty)/\mathrm{C}$ is given at

$$\frac{T-T_c}{T_c}=\begin{cases}\dfrac{\omega\tau_{p0}(1-c)}{1+c^2}\,,\ -\dfrac{\omega\tau_{p0}(1-c)}{2(1+c^2)} & ;\ 0\leq c<1\,,\\ 0 & ;\ 1\leq c\,,\end{cases} \tag{23}$$

as

$$[T_c(\varepsilon'-\varepsilon_\infty)/C]_{\max}=\begin{cases}(1+c^2)/2\omega\tau_{p0} & ;\ 0\leq c<1\,,\\ c/\omega\tau_{p0} & ;\ 1\leq c\,,\end{cases} \tag{24}$$

as shown in Fig. 1 and 3. At the Curie temperature, we have $[T_c(\varepsilon'-\varepsilon_\infty)/\mathrm{C}]=c/\omega\tau_{p0}$ and $[T_c\varepsilon''/C]=1/\omega\tau_{p0}$ as in Fig. 1–4.

Comparison of the experiment of $Ca_2Sr(C_2H_5CO_2)_6$[3] with the formula with c=0.308, $\varepsilon_\infty=3.0$ and $\tau_{p0}=2.2\times10^{-10}$ sec^{-1} is made in Fig. 5.

We can easily find that the Cole-Cole plot of the dispersion formula (14) is the arc of the circle as

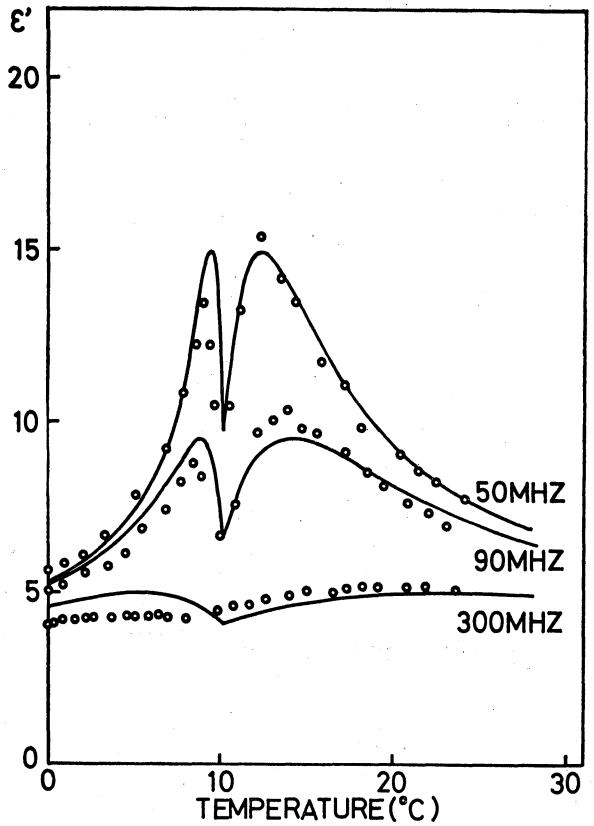

Fig. 5. Comparison of the experimental values (open circles) of $Ca_2Sr(C_2H_5CO_2)_6$[3] and the theory (solid lines) with c=0.308, $\varepsilon_\infty=3.0$ and $\tau_{p0}=2.2\times10^{-10}$ sec^{-1}.

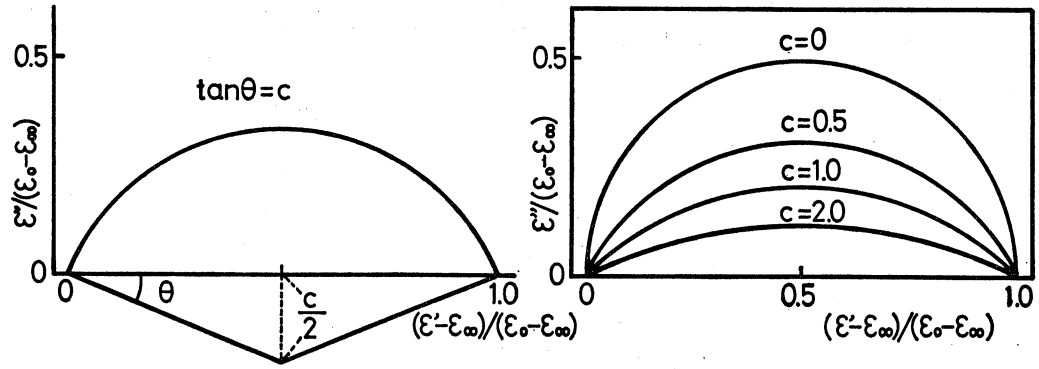

Fig. 6. Cole-Cole plots for various values of c.

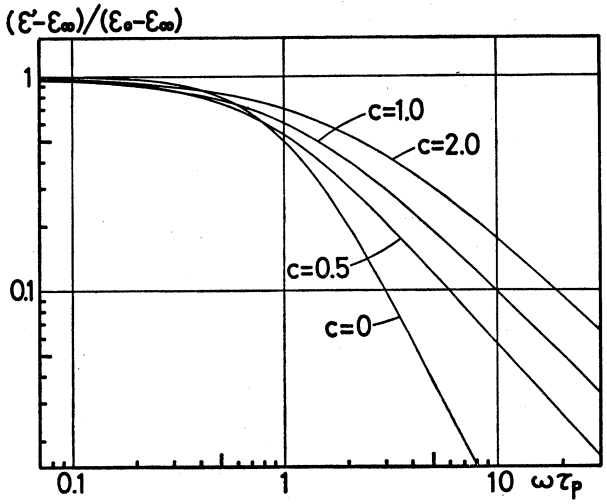

Fig. 7. The real dielectric constant versus the frequency at several values of c.

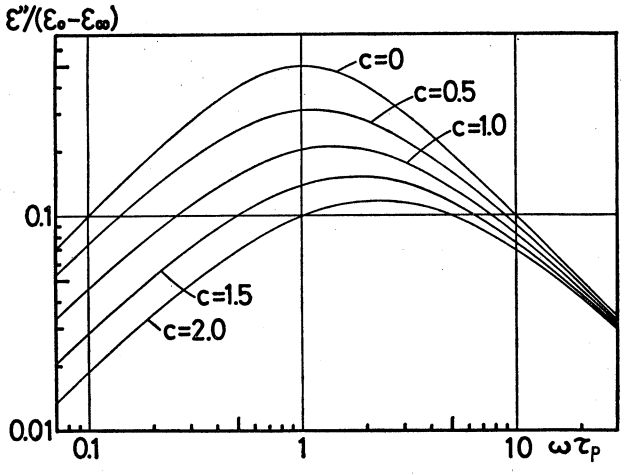

Fig. 8. The imaginary dielectric constant versus the frequency at several values of c.

$$\left\{\frac{\varepsilon'-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}-\frac{1}{2}\right\}^2+\left\{\frac{\varepsilon''}{\varepsilon_0-\varepsilon_\infty}+\frac{c}{2}\right\}^2=\frac{1+c^2}{4}. \tag{25}$$

The plots for various values of c are illustrated in Fig. 6. The frequency dependences of the real and imaginary parts of the dielectric constant are shown in Fig. 7 and 8, respectively. The imaginary dielectric constant $\varepsilon''/(\varepsilon_0-\varepsilon_\infty)$ takes maximum value:

$$[\varepsilon''/(\varepsilon_0-\varepsilon_\infty)]_{\max}=1/2(c+\sqrt{1+c^2}), \tag{26}$$

at the frequency of

$$\omega\tau_p=\sqrt{1+c^2} \tag{27}$$

as shown in Fig. 8. It is easy to see that our dispersion formula (14) is formally equivalent to Nakamura-Ishida's empirical formula (10) and the relation of them will be given in the next section. However, $\omega\tau_p$ dependence of ε' and ε'', which are shown in Fig. 7 and 8, are different from $\omega\tau$ dependence of ε' and ε'' of Nakamura-Ishida's formula, which have

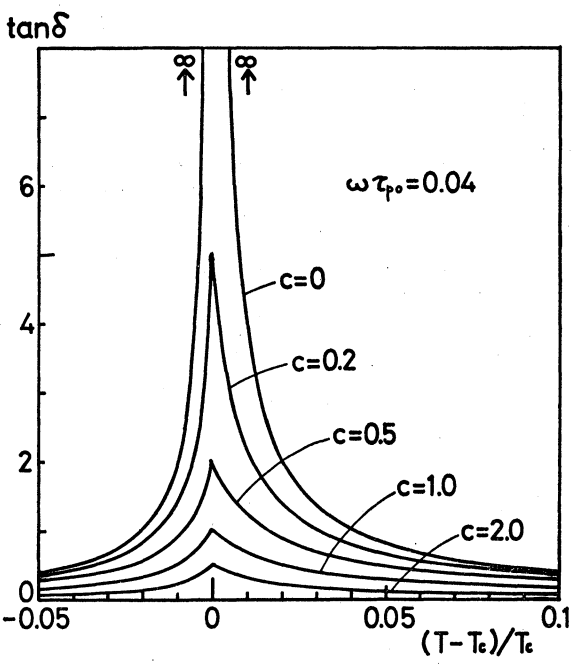

Fig. 9. The loss tangent versus temperature at several values of c.

been shown in Fig. 2 of ref. 19, respectively. These differences are attributable to the difference between τ_p and τ. The loss tangent $\tan\delta=\varepsilon''/\varepsilon'$ of the formula (14) is given by

$$\tan\delta = \omega\tau_p/\{1+(\omega+\omega_p)\omega_p\tau_p^2\}\,, \tag{28}$$

where ε_∞ has been neglected for simplicity. The loss tangent versus temperature at several values of c is shown also in Fig. 9. It is interesting that the loss tangent is finite, namely $1/c$, at T_c except for $c=0$ as in Fig. 9.

The calculations in this section, we have used that $\gamma=\Delta=\Delta'=1$ and the values of C, τ_{p0} and ω_{p0}^{-1} in the feroelectric phase are respectively the one half of the paraelectric phase's values. The paraelectric phase's values have been written in this section and Figures.

III. Discussion

We have studied the temperature and frequency dependences of the complex dielectric constant for extended order-disorder type ferroelectrics, employing the dispersion formula (14). The formal relation between our dispersion formula (14) and Nakamura-Ishida's empirical formula (10) can be obtained as

$$c = 1/\tan\left(\frac{\pi}{2}\beta_{NI}\right), \tag{29}$$

$$\tau_p = \tau/\sin\left(\frac{\pi}{2}\beta_{NI}\right). \tag{30}$$

By the definition (22), if the condition $\Delta=\Delta'$ is violated, the parameter c will depend on temperature.

The Cole-Cole plot of the dispersion formula (14) is the arc of the cricle (25), and the incline angle θ of the cricle is given by

$$\theta = \tan^{-1}c\,. \tag{31}$$

We compare the relation (31) with (8) and obtain

$$c = \tan\{\pi(1-\beta_{MY})/2\}\,. \tag{32}$$

It should be noted that the incline angle of experiments can be explained by the monodispersive formula (14) with the c. This indicates that the incline angle does not always measure the polydispersion. Recent experiment of $NaNO_2$[22] and $AgNa(NO_2)_2$[23] show that these crystals does not correctly obey the relation of critical indexes (18) but just above the transition point they conform to the relation of

$$\Delta = \gamma + 0.2\,. \tag{33}$$

This relation consists with the theory[24] of the kinetic Ising model. Below the transition point, the real dielectric constants of these crystals are small which can not be explained by our theory. These problems are under consideration.

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